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Study of alkali metal adsorption on reconstructed and unreconstructed Cu surfaces by HREELS

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The study of the stretching mode of Li, Na and K on various Cu surfaces show that the force constant of the adsorbate–surface bond depends neither on coverage nor substantially on the particular type of alkali atom. On the Cu(110) surface the spectra also infer that the (1×2) reconstruction may be induced by a local coverage less than 0.03 monolayers.

Vibrational spectroscopy of alkali overlayers has been successfully used to study the nature of the adsorbate–substrate bond and the mechanism of alkali-induced reconstruction on Cu surfaces [1–3]. These studies showed that for K and Na on Cu the stretching energies do not depend on coverage, θ, within 1 meV, while the dynamical dipole moment decreases by about one order of magnitude as a function of θ. Moreover a new dipole active surface mode was found on Cu(110) when the alkali metals induced the missing-row reconstruction [1]. This mode, detectable even at $\theta = 0.02$, points to local reconstruction at the lowest alkali coverages.

The independence of the stretching frequencies on alkali coverage is in agreement with Ishida's calculations for Na on jellium [4] and favours Ishida's picture of an alkali–surface bond which remains essentially covalent as the coverage changes from the dilute limit to a saturated single layer [5]. This picture is in contrast with the commonly accepted charge transfer model for alkali metal adsorption, according to which the bonding is mainly ionic at low coverage and metallic at high coverage [6].

The stretching frequencies of Na and K fall in the continuum of the bulk and surface modes of Cu. The coupling between overlayer and substrate modes can give rise to a broadening and a shift of the stretching peak in the EELS spectra. In order to evaluate these effects we have also studied the modes induced by Li on Cu(110), because the Li stretching energy is more than 5 meV above the maximum of the substrate continuum. In this paper we compare the Li results with those of the other alkali overlayers. We find that the Li stretching energy is shifted upwards by 2.5 meV with increasing coverage, and that this shift is explainable in terms of the dipole–dipole interaction and delocalization of the vibrational excitations related to the Li stretching mode. Upon reconstruction the energy of the Li–Cu stretching mode shifts downwards by about 2.5 meV. This occurs at coverages as low as 0.03, giving additional evidence for the presence of reconstructed regions even at the lowest coverages. The coverage dependence of the stretching energy indicates that the reconstruction does not occur through formation of dense islands. For the Na overlayer such a shift is less than our experimental error (about 1 meV) because in this case the Na stretching mode overlaps with the surface resonance of the (110) surface at Γ.

The HREELS spectra have been measured at a working pressure of 4×10^{-11} mbar within 30 min from the alkali dosing with an ELS 22 spectrometer and a resolution set at 4–5 meV. The spectra

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were recorded in the specular geometry with a primary electron energy of 2 eV and an incidence angle of 60°. The alkalis were dosed from a well outgassed SAES dispenser and the absence of contamination was checked with HREELS and AES. The spectra of alkalis on the unreconstructed Cu(110) surface were taken at 90 K after dosing at the same temperature. The alkali-induced reconstruction was obtained by annealing to 220 K after dosing at low temperature or by dosing the sample at 300 K. No changes were detected in the HREELS spectra after cooling the sample from 300 to 90 K. The alkali coverages were determined using AES and LEED as explained elsewhere [1,3]. θ is reported here as the ratio between the number of alkali atoms and that of Cu atoms on the unreconstructed surface.

Fig. 1 compares the energy loss spectra of Li and Na overlayers on reconstructed and unreconstructed Cu(110). On the unreconstructed surface (90 K) Na induces a single peak at 18 meV, the energy of which stays constant when the coverage is varied. When the surface reconstructs (300 K) a new peak appears at about 11 meV. Here again the energies of both structures do not depend on coverage, while the intensities vanish together in the high θ limit. In contrast to this, the Li spectra show a single strong peak in the range 33–38 meV (Li–Cu stretch) and a broad structure at about 18 meV both at 90 and 300 K. Moreover, the energy of the stretching mode increases with coverage by about 2.5 meV in both cases.

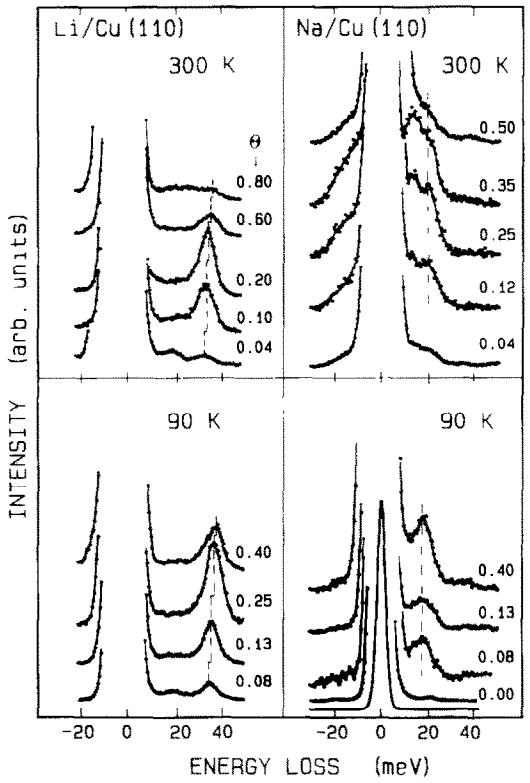

Fig. 1. Energy loss spectra of Li and Na on Cu(110) at 90 and 300 K (reconstructed 1×2 surface) for different coverages, θ. The spectra have been amplified by a factor of 40 with respect to the elastic peak shown in the lower left panel.

The energies and the intensities of the structures of fig. 1 are plotted in fig. 2 as a function of coverage. These data have been obtained by fitting the elastic and inelastic peaks in the spectra with gaussians. Clearly evident is the different behavior of the Li and the Na overlayers.

We begin our discussion with the Li data, since the interaction of the stretching mode with the substrate modes, which extend from zero to 30 meV, should be weak in this case. The coverage dependence of the energy and of the intensity of the stretching mode at 90 K follows the typical trend produced by the dipole–dipole interaction [7]. Theoretical calculations show that the dynamical dipole moment of the alkali adatoms decreases by about a factor of two on going from the lowest coverage to the saturated layer [8]. Fig. 2 shows the calculated shift of the stretching mode induced by the dipole–dipole interaction, assuming that the dynamical dipole moment decreases linearly from $q^* = 0.9e$ (dashed line) and $q^* = 0.5e$ (dotted line) at zero coverage to 50% of this value at saturation, where e is the electronic charge. It is also assumed that the electronic polarizability is $\alpha = 2 \times 10^{-23}$ cm^3 [9].The assumed linear dependence of the dynamical dipole moment is not jusified by theoretical calculations, but only mimics the coverage dependence of the static dipole moment [4]. The same parameters are used to evaluate the coverage dependence of the intensity of the loss peak and the result for $q^* = 0.5e$ is shown in fig. 2 as a dotted line line. The curve for $q^* = 0.9e$ would be three times higher. The value $q^* = 0.9e$ which gives a good fit of the experimental data for the energies is about twice that esti-

mated theoretically, while $q^* = 0.5e$, which is closer to the calculated value, explains only 1/3 of the observed shift, but is consistent with the loss intensities.

In order to fit the 300 K data we have assumed that in this case the dynamical dipole moment of the saturated layer is 30% of that of the single atom. The misfit at the lowest coverages can be attributed to small changes in the adsorption geometry as the reconstructed regions merge for increasing coverage.

The theoretical estimate $q^* = 0.5e$ leaves a 1.5–2 meV shift to be explained. There is another effect which causes an upward shift of the stretching frequency with increasing coverage even if the force constant of the alkali–surface bond and the adsorption geometry remain constant. It results from the change of the stretching mode from a localized vibrational excitation in the zero coverage limit to a delocalized surface mode at full coverage. This transition can also be seen as a change in the reduced mass of the Li–surface system and a change in the coupling between the surface modes as the number of Cu surface atoms responding to the motion of a Li atom changes. A preliminary model calculation shows that this effect can give rise to 1–2 meV shift in the case of lithium and a smaller shift in the case of Na and K [10].

The same mechanisms responsible for the energy shift of the Li peak should also operate in the Na overlayer. Here, however, the total shift induced by the dipole–dipole interaction should be less than 1 meV even if q^* were $1e$ [10]. Moreover, the Na stretching energy (18 meV) is very close to that of the surface resonance of the Cu(110) surface (19.5 meV) [11] and the two modes, having the same symmetry, strongly interact. Therefore the energy of the observed loss peak, produced by the coupling of the two modes, is less sensitive to changes in the potential felt by the alkali atom [10]. This also explains why the 18 meV Na peak does not shift upon reconstruction, on the contrary to what is observed for Li. The

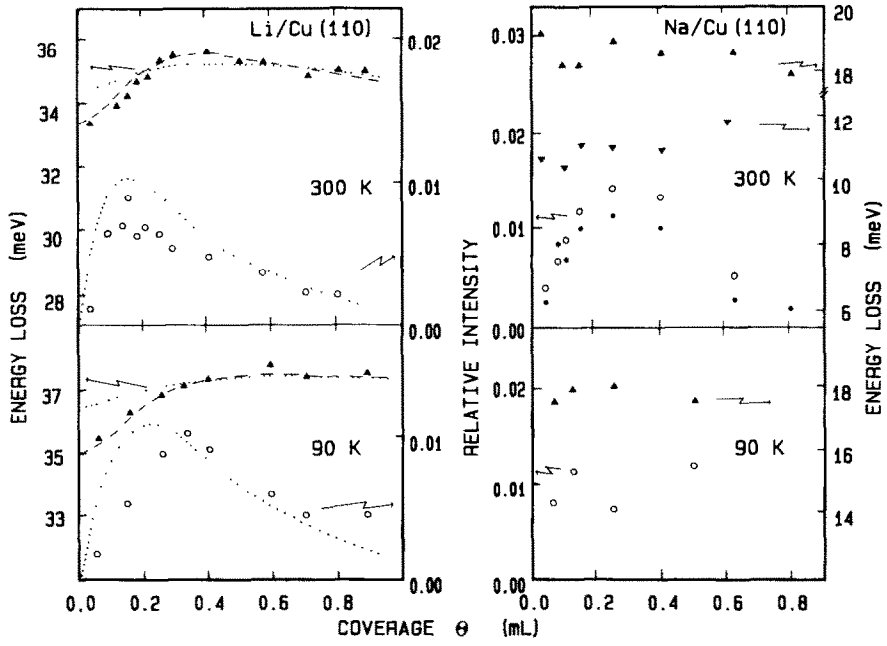

Fig. 2. Energies (triangles) and intensities (circles) of the stretching peaks in the loss spectra as a function of coverage, θ. The inverted triangles and the dots in the upper left panel refer to the Cu surface mode at 11 meV. The dotted (dashed) lines show the calculated coverage dependence of the intensities and the energies taking into account the dipole–dipole interaction and assuming $q^* = 0.5e$ ($q^* = 0.9e$) (see text).

(1×2) reconstructed (110) surfaces of fcc metals have a surface resonance at Γ which derives from that present on the unreconstructed surfaces and has nearly the same energy [12]. This resonance could lock the energy of the peak observed in the loss spectra. The coupling of the Na mode with the substrate mode is also attested by the linewidth of the loss peak. This linewidth is about 10 meV (which corresponds to an intrinsic width of 8 meV) for Na both at 90 and 300 K, while it decreases to 6 meV (corresponding to an intrinsic width of 4 meV) for Li.

The fact that the force constant of the alkali–substrate bond shows a negligible coverage dependence while the alkali metal adsorption energy is strongly dependent on coverage [6], as testified by a pronounced shift of the alkali desorption temperature for increasing θ, means that the curvature of the energy versus alkali–substrate distance at the equilibrium position and the depth of the minimum of this curve relative to the value of the energy at infinite distance have different coverage sensitivity. This can be understood on the base of Ihida's calculations [4]: the curvature at the equilibrium position is mainly related to the charge distribution and the electrostatic field in the region between the substrate and the alkali plane, which are only weakly dependent on θ. On the contrary, the depth of the minimum, i.e., the work necessary to bring the alkali atom far from the surface, is also quite sensitive to the alkali atom–surface interaction at large distance from the surface, i.e., to the charge distribution and the electrostatic field on the vacuum side of the alkali plane. In this region of space the charge depletion is strongly coverage dependent and causes a large change in the electrostatic field and in the work function for increasing θ [4].

Another striking difference between the Li and the Na cases is the presence of a broad peak at about 18 meV in the former, both at 90 and at 300 K, and of a sharp peak at 11 meV in the latter when the surface is reconstructed. The Li-induced 18 meV peak derives from the 19.5 meV resonance of the clean surface which becomes highly dipole active in the presence of alkali atoms. A preliminary calculation shows that the intensity, the lineshape and the energy position of this loss depend strongly on the ratio between the force constant of the bonds of the Li atom with the first and the second Cu layer [10].

The 11 meV peak of the Na overlayer derives from the S_3 mode in the Γ–Y direction of the Brillouin zone of the clean (1×2) surface which couples with the vertical motion of the Na atoms [1]. Its intensity should decrease by about a factor of 10 when the stretching energy of the alkali atom changes from 18 to 35 meV [10]. This fact, plus the slightly worse resolution we obtained with the Li overlayer, explains why the 11 meV mode is not detected in the spectra of the Li/Cu(110) system.

The stretching energies of Li, Na and K (33–36, 18 and 13.7 meV, respectively) scale as the inverse of the square root of the atomic masses within 10%. This result implies that the force constant of the adsorbate–substrate bond is also rather insensitive to changes in electronegativity and size of the adsorbed atoms.

The downward shift of the Li stretching energy upon reconstruction arises from the changes in coordination and bonding geometry caused by adsorption in the [110] troughs of the (1×2) surface [13]. The direction of this shift and the similarity of the energy versus coverage curves at 90 and at 300 K do not agree with the hypothesis that at low coverage the reconstruction occurs through formation of relatively dense Li islands [13]. If this were the case the stretching energy would be less coverage dependent in the range 0–0.15 ML at 300 than at 90 K (temperature at which no islanding should occur).

In conclusion we have shown that the shift of the Li stretching energy on Cu(110) as a function of coverage can be accounted for by the dipole–dipole interaction and by changes in the coupling between the surface modes. Therefore Cu–Li force constant does not change appreciably with the Li surface density. This finding is in agreement with previous studies of Na and K on Cu surfaces and with Ishida's calculations.

The shift of the Li stretching peak and the rise of a new Na-induced loss upon annealing at 220 K at coverages as low as 0.03 ML confirm the presence of reconstructed regions even in the low density limit, when no $(1 \times n)$ LEED pattern is

observable, and favours local mechanisms for the alkali-induced reconstruction of the (110) surfaces of the fcc metals.

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